Research Grant Proposal
Environmental Research Program
Wisconsin Focus on Energy

Measuring Vertical Fluxes of Gaseous Elemental Mercury near Coal-Fired Electric Utility Plants and Other Major Sources in Wisconsin Using Relaxed Eddy Accumulation

A) Abstract

The Department of Natural Resources is requesting funds to develop and deploy a system to measure gaseous elemental mercury fluxes in the vicinity of coal-fired electric utility plants and other major sources using a conditional sampling method called Relaxed Eddy Accumulation. The vertical flux in gaseous elemental mercury (Hg^0) is an important component of the overall mercury loading to land and water surfaces because of the complex deposition and re-emission processes involving atmospheric mercury. The Department is currently developing a rule to control mercury emissions released to the atmosphere from coal-fired electric utility plants and other major sources. To support evaluation of the rule, the Department is developing a modeling system for Wisconsin and the Great Lakes region. The vertical flux of mercury near land surfaces needs to be quantified to more accurately model the potential impact of mercury emissions to the state from coal-fired electric utility plants and other major sources.

Relaxed Eddy Accumulation (also called conditional sampling) is a micrometeorological technique that is based upon the principle that the flux of any scalar is proportional to the difference in concentrations between upward and downward-moving air parcels multiplied by the vertical wind speed's standard deviation. Recently, Cobos *et. al* (2002) extended an initial application of conditional sampling (Beverland, *et al*., 1996) to successfully measure fluxes of mercury from agricultural soils. The Department is proposing to develop a transportable conditional sampling system to capture the target pollutant mercury on gold adsorption traps. A sonic anemometer to measure the vertical wind speed would then be employed to estimate bulk vertical mass transport.

The first phase of the project would be to assemble and test the proposed sampling system. This testing phase would include optimizing parameters for the measurement of vertical mercury fluxes. Phase two of the project would be to deploy the sampling system at several locations in Wisconsin that are near relatively significant sources of atmospheric mercury emissions (i.e., coal-burning electrical power generating facilities, a chlor-alkali plant, recycling facilities), as well as urban and remote background locations. The initial flux monitoring would utilize gold traps to collect the total mercury (i.e., reactive and non-reactive). In the third phase of the study, the use of potassium iodide coated denuder tubes would be tested to determine if the flux of reactive gaseous mercury is measurable. This proposal is seeking funds for the purchase of monitoring equipment, laboratory services, and staff time. A total funding of $39,500 is being requested for use in the 2003/2004 calendar years.

B) Program Interest Area to be addressed

This proposed study would address the interest area of the Focus on Energy's Environmental Research Program entitled "Mercury in Wisconsin" (category B of "Electrical Generation and Human Health"). The Department is currently developing a system to model mercury emissions transport and deposition to Wisconsin and the Great Lakes region. The modeling system is being developed to assess the impacts of the Department's proposed air mercury rule to reduce mercury emissions from electric utility plants. The proposed mercury flux research data would be incorporated into the Department's mercury modeling effort to more accurately model the impacts of the Department's proposed air mercury rule on mercury deposition in Wisconsin. Cobos, *et.al.,* (2002) stated that "..it is important to accurately quantify Hg^0 fluxes.." in part because "..Hg^0 sources can be widely separated from areas of deposition.." due the pollutant's "..volatile nature and long atmospheric residence time..".

If this project is not realized, it could be inferred from Cobos, *et.al.*, (2002) that the absence of any Hg^0 flux data may impair the accuracy of the Department's mercury modeling results. This consequence may occur because if the modeling does not adequately account for local vertical exchanges of Hg^0 between the atmosphere and surface.

C) Usefulness and Value of Project Results

Cobos, *et.al.*, (2002) point out that it is important to determine the complicated fate of atmospheric gaseous elemental mercury (Hg^0) emissions. This assessment can be accomplished by accurately measuring the atmospheric fluxes in ambient Hg^0 that emanate directly through the air from anthropogenic sources (such as coal-fired electric utility plants) and the Hg^0 re-emitted from surfaces such as water, soil and geological formations. The proposed sonic anemometer's measurements of downward or upward-moving air near the ground would help yield estimates of bi-directional fluxes in the Hg^0. It is anticipated that the ambient Hg^0 levels would be dominated by the contributions made directly from the atmosphere.

The geographical focus of this proposed study would be Hg^0 flux monitoring in the vicinity of several coal-fired power plants in Wisconsin, which collectively comprise the State's single largest category of anthropogenic Hg emissions. Measurements of Hg^0 flux would also be conducted at a different type of large Hg source, as well as at a remote site (the latter location to establish a background Hg^0 flux).

The Hg^0 flux measurements of derived from this proposed field study would improve the accuracy of the Department's effort to model mercury deposition to Wisconsin. The Department's mercury modeling project is designed to estimate the impact of a proposed Department rule to reduce the emissions of mercury released to the atmosphere from coal-fired electric utility plants. Consequently, employing the Hg^0 flux data in the modeling effort would more accurately assess the potential impact of the proposed Hg control rule.

The Department is also monitoring ambient mercury at selected location to assess the impacts of nearby sources. As a part of this work and prior to the start of the flux measurement field study, the Department will evaluate ambient mercury concentrations at the monitoring sites for the field study. This monitoring evaluation will include initial monitoring surveys with a LUMEX monitor. The surveys will then be followed with short term (15 to 30 days) monitoring studies with a Tekran 2537a analyzer. As a follow-up to this project we hope to evaluate relationships between measured Hg^0 fluxes and mercury concentrations in precipitation collected at near-by MDN sites.

D. Soundness of project methods

We propose to assemble a transportable system to conduct gas flux measurements using the relaxed eddy accumulation (REA) technique, also called conditional sampling. Once assembled and tested, the system will be used in a field study to measure mercury vapor fluxes. The primary goal of the proposed field study will be the verification of the flux parameters used in the Department's mercury prediction computer model. A second goal will be an examination of the influences that may affect mercury flux rates.

The REA method has been used extensively in measuring the gas fluxes for a number of compounds. Reported studies successfully using REA include Beverland et al (1996) for measuring methane and nitrous oxide fluxes, Zemmlick et.al (2002) for dimethyl sulphide fluxes , Zhu et. al. (2000) for ammonia fluxes, Valenti et al (1997) for biogenic VOCs fluxes, and Cobos et al (2002) for mercury vapor fluxes. The principle of the REA measurement is the collection of air samples on two pathways. The first

pathway collects a sample when the vertical (i.e., "z") wind component is moving upward and the second path when the z wind component is moving downward. The difference in the concentration between the two wind paths is mathematically converted to the target pollutant (e.g., mercury) net vertical flux. The components of all REA systems are similar and are comprised of three elements. The system must have a sensor to measure three-dimensional winds, a control system to analyze the wind data and execute sampling decisions based on the wind direction, and finally a system to collect and measure the concentrations of the target compound. Studies have made the concentration measurement in the field using real-time analyzers (Beverland and Cobos). Other studies have also collected samples for analysis at an analytical laboratory.

An REA system would be assembled using commercially available equipment. Measurement of three-dimensional winds would be made using a sonic anemometer. The sonic anemometer makes a measurement of wind speed and direction detecting changes in an acoustic signal. The sonic anemometer has no mechanical components thus allowing the measurement of rapid fluctuation in the wind signal. The Wisconsin monitoring staff currently uses sonic anemometer technology to conduct two dimensional wind measurements at selected air monitoring stations. Data logging and sampling control system would be assembled using surplus data loggers. The WDNR Air Monitoring program has extensive experience in data logging and control systems. It currently operates a network over 50 monitoring sites where data is electronically collected and recorded. At enhanced ozone monitoring stations and at air toxics monitoring stations computer programs written by Department staff are used to control specialized sampling systems. The final element of the REA sampling system would be the sample collection system assembled by Department air monitoring technical staff. Department staff has extensive experience in the assembly of sampling systems, Allen, Miller, and Leair (1996, 1994).

The REA system would collect mercury gas samples on commercially prepared gold coated quartz sand traps (Brooks Rand LLC) for analysis at the Wisconsin State Laboratory of Hygiene. These same type of traps have been used by the Department for ambient mercury monitoring studies and in particular to collect mercury from an airborne sampling platform. An evaluation by Grande and Allen found the gold trap could successfully be used for the collection and measurement of mercury vapor at nanogram per cubic meter concentrations.

***References**:*

Allen, M.K., Miller, E., and Leair, J., 1994: Evaluation of an intelligent multi-canister/ multi-cartridge sampler for the collection of ozone precursors ", *Proceedings of the 1994 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants*, VIP-39, AWMA:Pittsburgh,:205-210.

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Beverland, I.J., D.H. Oneill, S.L.Scott and J.B. Moncrieff, 1996: Design, construction,and operation of flux measurement systems using the conditional sampling technique. Atmospheric Environment 30: 3209-3220.

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Valentini, R., S. Greco, G. Seufert, N. Bertin, P. Ciccioli, A. Cecinato, E. Brancaleoni, and M. Frattoni, 1997: Fluxes of biogenic VOC from Mediterranean vegetation by trap enrichment relaxed eddy accumulation. Atmospheric Environment 31: SI229-238.

Zemmelink, H.J., W.W.C. Gieskes, W. Klaassen, H.W. de Groot, H.J.W. de Baar, J.W.H. Dacey, E.J. Hintas, and W.R. McGillis 2002: Simultaneous use of relaxed eddy accumulation and gradient flux techniques for the measurement of sea-to-air exchange of dimethyl sulphide.

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E. Statement of Work Tasks: Objectives, Methods, Deliverables, Persons Responsible and Time Schedule

Task 1: Select the WDNR monitoring site to be used and identify target meteorological conditions for flux measurements.

- *Objective:* Select the monitoring sites at which the REA system would be used. Selected site must have available support equipment including a shelter and electrical power. Determine meteorological conditions where the power plant plume or other selected source would significantly impact the monitoring site. Also identify target meteorological conditions for supplemental flux measurements. These supplemental conditions include time of day, precipitation events, and surface ground cover.

- *Methods:* Use several years of local wind direction data to construct a climatological wind rose for the area surrounding the source. Analyze the wind rose to recognize prevailing downwind directions for plume transport. Identify meteorological conditions that place the site locations in the area of these prevailing plume paths. Prioritize the candidate site locations considering factors such as the relative likelihood of being in the plume's path, distance from the plant, and accessibility. Select sites and target meteorological conditions based upon all of these considerations. Develop a monitoring plan that includes a forecasting plan for target meteorological conditions.

- *Deliverables:* A monitoring project plan for the field study would be developed. The plan would include a forecasting protocol to select target meteorological conditions. The monitoring plan would be incorporated in appendix form into the project's progress reports and final report.

- *Persons responsible:* Bill Adamski will lead this planning effort. Mark Allen will assist providing technical assist with the operational details of the plan.

- *Completion time* (from project initiation): 3 months.

Task 2 : Procure component parts for the REA monitoring system/ assemble the REA monitoring system/ hire / train part-time operating technicians and establish laboratory analysis contracts and support services.

- *Objective:* While task one is being completed, also obtain the necessary components to assemble a Relaxed Eddy Accumulation measurement system. Assemble and test the system to demonstrate that it can accomplish the goal for the field monitoring. Establish contracts for required analytical services. Hire support personnel.

- *Methods:* Follow standard State of Wisconsin procedures for obtaining these resources.

- *Deliverables:* A REA monitoring system that is tested and ready for use in Task 3. An operating staff trained in the operation of the REA system. A detailed description of how this task was conducted would be incorporated into the project's progress reports and final report.

- *Persons responsible:* Mark Allen will lead the efforts to develop the REA monitoring system.

- *Completion time* (from project initiation): 4 months.

Task 3: Commence monitoring field study.

- *Objective:* Conduct field monitoring to measure mercury vapor fluxes at the selected monitoring locations and under target meteorological conditions.

- *Methods:* The monitoring project will be conducted using the monitoring plan developed in Task 1 to guide its operation. The field study will conduct a base-line monitoring project at all monitoring stations. Targeted meteorological conditions may be monitored at selected sites. A detailed description of how this task was conducted would be incorporated into the project's progress reports and final report.

- *Deliverables:* A project database containing all field and laboratory data collected for the project. This will include air concentrations and meteorological measurements collected at monitoring sites.

- *Persons responsible:* Mark Allen will lead the field monitoring effort. Monitoring staff will conduct the field measurements.

- *Completion time* (from project initiation): 16 months.

Task 4: Calculate the mercury vapor fluxes and evaluate the field study measurement data.

- *Objective:* Validate and review field study data to determine that the data meet the data quality objectives of the monitoring project. Using the field study measurement data calculate the mercury vapor fluxes. Review the data flux measurement and determine if the calculated data meets project goals. If necessary make adjustments to the field monitoring plan to meet project goals.

- *Deliverables:* A detailed description of how this task was conducted along with relevant figures and tables would be incorporated into the project's progress reports and final report.

- *Person responsible:* Mark Allen will lead the effort to validate field data. Bill Adamski will lead the effort to calculate mercury vapor fluxes and evaluate the flux data.

- *Completion time:* Field data will be reviewed in the first 6 months of the study. A final report will be made within 3 months of the availability of the final measurements.

Task 5: Evaluate the REA measurement system for use in collecting RGM Fluxes.

- *Objective:* Test the REA system assembled in Task 2 for use in collecting RGM fluxes.

- *Methods:* Potassium iodide coated denuders will be used in place of the gold traps in the REA measurement system. Sampling parameters will be optimized to collect samples for RGM fluxes.

- *Deliverables:* A appendix to the monitoring field plan outlining the monitoring parameter and a monitoring plan to conduct RGM fluxes. Monitoring data will be added to the project database table and evaluated. A detailed description of how this task was conducted along with relevant figures and tables would be incorporated into the project's progress reports and final report.

- *Person responsible:* Mark Allen.

- *Completion time:* To begin within 3 months of field study completion and be completed 3 months thereafter.

Task 6: Reporting and information transfer.

- *Objective:* Provide information on the project status, data and analyses to the funding agency on a consistent, continual basis.

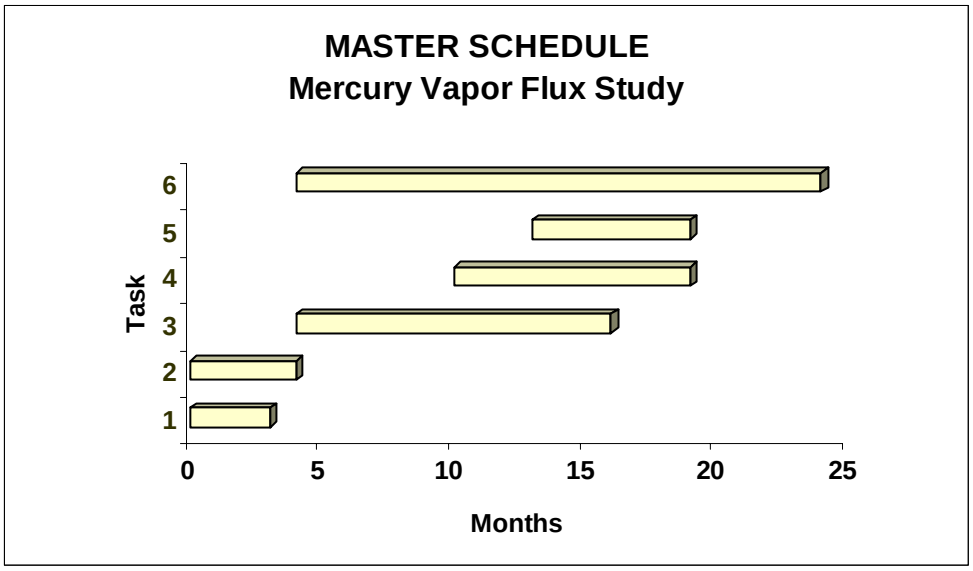
- *Methods:* Quarterly status reports of no more that two type written pages will be provided. A final report on the project will be completed within 24 month after the project is initiated. Based upon the significance of the findings, a peer-reviewed research paper (or papers) may be written for publication in an appropriate scientific journal.

- *Deliverables:* The project documentation described in the "methods" section.

- *Persons responsible:* Mark Allen, Bill Adamski, Tom Sheffy, and Larry Bruss.

- *Completion time:* At specified intervals during the lifetime of the contract.

Master Schedule. The diagram below shows the overall master schedule for the project. All tasks will be completed within 24 month after the project is initiated. The tasks to be completed are listed as follows:



Task 1: *Select monitoring sites and identify target meteorological conditions for flux measurements.*
Task 2: Assemble and test the REA monitoring system/ hire and train part-time operating technicians and establish laboratory analysis contracts.
Task 3: Monitoring field study.
Task 4: Calculate the mercury vapor fluxes and evaluate the field study data.
Task 5: Evaluate the REA method for collecting RGM Fluxes.
Task 6: Reporting and Information transfer.

F) Management Plan and Qualifications

Organizational List

Key Personnel (listed alphabetically)

Bill Adamski (WDNR Air Management Data Analyst)
Conduct wind rose assessment and flux data analyses. Evaluate measured and modeled flux parameters. Assist in selecting monitoring site.

Mark Allen (WDNR Air Monitoring Chemist)
Manage assembly and testing of REA system, field monitoring study, and initial data validation.

Larry Bruss (Chief, WDNR Regional Pollutant and Mobile Sources Section)
Act as the Associate Principal Investigator. In this capacity he would expedite resources for the field study and data analysis. Mr. Bruss will also present the study data to the Air Programs Mercury Data Analysis Team for use in the team's modeling effort.

Tom Sheffy, Ph.D. (Chief, WDNR Air Monitoring Section)
Act as the Principal Investigator and provide general oversight and guidance for the project.

Support Personnel

David Grande (WDNR Air Monitoring Chemist)
Assist Mr. Allen in testing and training the field monitoring staff.

Part-time Field Technician (to be hired) to operate the REA sampling system during the filed study, (maintenance, QA, collecting samples and shipping them to WLSH, etc..).

Contractors

Laboratory analysis for mercury will be conducted at the Wisconsin State Laboratory of Hygiene. The laboratory of Hygiene provided mercury analysis to the Wisconsin DNR for precipitation samples collected by the Wisconsin Deposition Monitoring network which operated until 1999. The laboratory provides analysis of gold traps used in air samples collected using the Wisconsin DNR's aircraft sampling program.

Resumes of Key Personnel
See attached MS-Word file entitled "wdnr_proposal_hg_powerplant_focus_on_energy_resumes.doc".

Related Projects

The Wisconsin Department of Natural Resources has great interest in the environmental impacts and atmospheric sources of mercury. The Department's air monitoring program currently operates five air monitoring station that collect precipitation samples and are part of the National Mercury Deposition Network(MDN).

Wisconsin together with Michigan and Minnesota operates a Mercury Analysis trailer equipped with two Tekran 2537a mercury analyzers. The mercury trailer is used for short term monitoring projects to investigate and characterize source emissions from mercury sources in the three states.

The Department has lead in an effort to make mercury measurement from upper altitudes through the collection of mercury samples from an aircraft sampling platform.

G) Project Budget

Duration of Project: 24 months

BUDGET SUMMARY

Cost Category	See Budget Detail	Amount
Personnel including fringe benefits	A	$19,504
Travel	B	$1,000
Contractual	C	$13,781
Equipment	D	$16,000
Supplies	E	$2,200
Other Direct Costs	F	$1,000
TOTAL PROJECT BUDGET		**$54,485**
Total Cost Share/Match (27.5% of total budget)	G	**$14,985**
TOTAL GRANT FUNDING REQUESTED		**$39,500**

BUDGET DETAILS

Budget Detail	Cost Category	Amount
A	Personnel	
	1. FTE Meteorologist, 60 hours @ 23.516	$1,411
	Fringe and Indirect	$980
	2. FTE Chemist, 100 hours @23.416	$2,342
	Fringe and Indirect	$1,626
	3. FTE Chemist, 120 hours @18.922	$2,271
	Fringe and Indirect	$1,577
	4. LTE Field Staff, 450 hours @14.124	$6,356
	Fringe and Indirect	$2,941
B	Travel	$1,000
C	Contractual	
	1. Wisconsin State Laboratory of Hygiene 275 analyses @50.11	$13,781
D	Equipment	
	1. Sonic 3-dimensional anemometer	$8,000
	2. Sample collection system (values, flow meter, control circuits)	$4,500
	3. Data logging and control system	$3,500
E	Supplies	
	1. Gold traps for Hg collection, 10 @120	$1,200
	2. Miscellaneous (upgrades to monitoring sites)	$1,000
F	Other Direct Costs	
	1. Data analysis support (computer modeling)	$1,000
	2. Technical support (specialized fabrications)	$1,000
	TOTAL PROJECT BUDGET	$54,485
G	Cost Share/Match (27.5%)	$14,985
	TOTAL GRANT FUNDING REQUESTED	$39,500

Comments on Budget:
The WDNR would provide considerable cost-sharing support to this project in the form of in-kind contributions of personnel time and equipment. These contributions would include completing the following tasks:

- Efforts in conducting the monitoring site evaluation and determining target meteorological conditions (Task 1),
- Efforts to assemble and test the REA monitoring equipment, including evaluation of component parts to insure specifications for the sampling system are met. (Task 2),
- Use of surplus data logging and sample collection equipment used to assemble the REA monitoring system.(Task 2),
- Conducting the field study including use of shelters at existing air monitoring stations (Task 3),
- Developing a database to contain all project data (Task 3),
- Calculating the vapor fluxes and validating the data(Task 4),
- Use of WDNR denuder sampling system for RGM sampling including preparation of the denuder sampling surface (Task 5)
- Report preparation and information transfer (Task 6),

The Request for Proposals (RFP) by the Focus on Energy Environmental Research Program states that cost-sharing of at least 25% is desirable. The WDNR's proposed budget includes a 27.5% in-kind contribution.

H) Letters of commitment or support. The proposed project will be conducted completely within the Department of Natural Resources.

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